When one heats a-Si:H nanoparticles obtained by PECVD in dry air, one observes the oxidation of the material just in the temperature range where dehydrogenation occurs (Fig.1). In fact, elementary analysis, complemented by mass gain measurements and IR spectroscopy, leads to the conclusion that the oxygen atoms are incorporated on the fresh silicon dangling bonds leaved behind by the hydrogen atoms. The oxygen uptake is quite fast in view of the fact that reduction of the oxygen partial pressure in the furnace by a factor of 20 reduces the oxidation by a factor of two, only (Fig.2). Although this effect has been well characterized in a-Si:H nanoparticles [1], it works on a-Si:H thin films, too, provided that the Si-H groups are not dissolved in the Si network but in the form of Si-H$_2$ or (Si-H$_2$)$_n$. In fact, it has been observed recently by independent authors on a-Si:H films [2].

The enhancement of the oxidation rate during dehydrogenation makes possible to control where oxidation takes place simply by controlling the hydrogen content. This can be done with nanometric resolution by means of an electron beam or at submicrometric resolution with an UV beam. Both radiations can break the S-H bonds and locally reduce the H-content (the electron beam of a microscope has been used recently to obtain Si dots in a SiO$_2$ matrix [3]). If local dehydrogenation is done in air, the scanned region will be oxidized. This process will be done with an environmental SEM where the electron beam reaches the sample surface that is surrounded by gas at near atmospheric pressure. If one wants to draw an active nanometric region with the electron beam, then it must be scanned in vacuum. The scanned region now obtained will become dehydrogenated and, consequently, less prone to oxidation. Now, oxidation of the thin film by thermal annealing will result in a Si region surrounded by silicon oxide. The Si region can become polycrystalline if the annealing temperature is high enough.

In this communication, the results obtained with a-Si:H nanoparticles will be revised and preliminary oxidation experiments done on a-Si:H thin films grown at several substrate temperatures will be presented. In particular, the experiments show that oxidation is more pronounced in the films grown at lower substrate temperature. The weak intensity of the IR signal in the region of the TO$_4$ mode in silica (Fig.3) indicates that, although oxidation takes place at low temperature during dehydrogenation, oxygen incorporation is limited to a thin region near the free surface.

A systematic investigation has been undertaken in order to better control the low-temperature oxidation phenomenon. The aim is to develop a new lithographic technique that applies to a-Si:H thin films and allows patterning active and passive regions by localized oxidation. In contrast with conventional lithography, where the beam modifies locally the reactivity of a thin resist film, in our proposal it is the active material itself (a-Si:H) that is modified.
References